Hydrate formation and dissociation in field samples, DOE-FEAB111

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Introduction:

The goal of this research is to characterize the thermodynamics and kinetics of natural gas hydrate formation and dissociation and biogeochemically characterize MH containing sediments. Characterization of samples from ODP Leg 204 is the primary focus with minor efforts on February 2002 coring of Mallik. Experiments are being conducted in the ORNL Seafloor Process Simulator at the ORNL hydrate research facility. Microbiological enrichments and time course characterizations are being conducted with properties correlated with hydrate thermodynamic and kinetic properties.

Recent Highlights:

1. Biological methane production from ODP Leg 202 cores are nearing their final incubation point after more than three months with one set of incubations under ambient conditions, and two at near in situ temperatures of 4C. Some are enriched with acetate, hydrogen and or methanol. These tubes may be in stark contrast to those from Masllik where results revealed considerable production of carbon dioxide from radiolabeled 14C-2-acetate but no radioactive methane (sensitivity of 200 dpm from 10,000,000 dpm of added 14CO2 or 14-acetate). Similarly, no increase in the methane concentrations within the headspace of test tubes were detected (sensitivity of ~0.1%) during the >3 month time course experiment of the Mallik samples but considerable methane and radioactive methane are anticipated formt he ODP cores. Results are being corroborated those of R. Colwell amd M. Delwiche (INEEL) and other investigators.

2. A new procedure/method for enhancing the nucleation of hydrates was recently discovered as part of this work. The discovery leads to a 10- 20- fold improvement in the amount of overpressure required for nucleation, from ~600 psi to ~30 psi. A draft patent disclosure is being reviewed and it should be submitted within a couple of weeks. The new procedure was not expected from a review of the literature and the results were startling. In the range of 3-6 C nucleation pressures greater than 1200 psi are customary for nucleation to occur in the SPS. Similar to smaller vessels as noted in the literature there a significant memory effect is noted upon repeated formation of hydrates. If hydrates are dissociated and then reformed within hours a memory effect is obsereved and nucleation often occurs at far less overpressure. For example, in fresh water nucleation overpressures of ~600 psi are typical whereas if hydrates are formed again using the same water (even if there is a 24 hr lag time) the overpressure required to form hydrates is typically 200-300 psi. This memory effect represents a substantial energy savings from initial hydrate formation equilibria. Consequently any nucleation enhancer should lower the required overpressure far more than any observed memory effect. Our new process resulted in required overpressures of only 22 and 33 psi in two separate attempts with fresh water. This is nearly an order of magnitude better than nucleation

enhancement of the well known memory effect. This phenomenal successful nucleation enhancement procedure may be more scalable and less expensive though at least as effective as our procedure documented some three years ago.

3. The Marine Geology paper entitled "Sediment Surface Effects on Methane Hydrate Formation and Dissociation" authored by David Riestenberg, Olivia West, Sangyong Lee, Scott McCallum, and Tommy J. Phelps is officially In Press for a special Issue entitled "Geosphere-Bioshpere" hopefully in the March-April issue of Marine Geology.

Planned research:

1. Biogeochemical and microbiological characterization of the ODP-LEG 204 samples is underway and preliminary results will be available next quarter.

2. Thermodynamic and hydrate kinetic experiments are being planned for late 2002 or early January timeframe. Sufficient materials or high quality are preserved for the planned experiments.

3. Experiments are also planned for even further enhanced hydrate nucleation materials. In previously DOE-FE-GH program research a patent disclosure was filed. This second filing will add value to the first and lead to a great likelihood that enhanced nucleation can be scaled to levels appropriate for deep sea or deep subsurface applications. During the spring and summer 2002 DOE-GH workshops interest was expressed in the enhanced nucleation of hydrates, particularly low cost additives for drilling fluids. Experiments are planned for the SPS in late 2002 to verify the experiments performed in 1999 and then to prepare for the addition of such additives to bentonite drilling fluids and see if their presence at a few ppm still increases the rate and or the nucleation of methane hydrates at lower pressures and higher temperatures. Based on our knowledge of hydrate nucleation we have reason to suspect that our additives may perform better and at lower or comparable costs to lecithin additives currently used in the drilling industry.

4. Phelps is invited to participate in the International Pressure Coring Workshop sponsored by the ODP. The conference is in College Station, TX, Februarry 5-7, 2003 and the topic of the presentation will be on the SPS being an integral link to the accessing and R&D on cores recovered at temperature and pressure, exuded at temp and pressure and then examined in the native temperature and pressure regime.

Collaborators in this project:

R. Colwell and M. Delwiche of INEEL
Ocean Drilling Program, particularly Frank Rack.